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Steric effect of β-diketone in synergistic extraction of actinide(III) and lanthanide(III) with β-diketone +18-crown-6 ether/1,2-dichloroethane

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Abstract

Synergistic extraction of trivalent actinide ions, Am^{3+} and Cm^{3+}, and lanthanide ions, Nd^{3+}–Tb^{3+}, into 1,2-dichloroethane containing 18-crown-6 ether (18C6) and a β-diketone (HA); trifluoroacetylacetone (HTFA), 2-thenoyltrifluoroacetone (HTTA), benzoyltrifluoro acetone (HBFA), or 2-naphthoyltrifluoroacetone (HNFA), was investigated. The metal ion M(III) is extracted through one of two competitive extraction reactions which is either a synergistic ion-pair extraction (SIPE) of a cationic complex, $MA_2(18C6)^+$, or a synergistic extraction (SE) of a neutral complex, $MA_3(18C6)$. Steric hindrances due to the bulkiness of the substituent group of HA influence the predominancy of one of the competitive reactions, SIPE or SE. Large separation factors are obtained by SIPE of M(III) ions using HA with relatively small substituent groups. The steric effect can be interpreted by taking into consideration the configuration of the extracted complexes. © 1998 Elsevier Science S.A.

Keywords: Synergistic ion-pair extraction; Steric effect; β-Diketone; Crown ether; Actinide(III); Lanthanide(III)

1. Introduction

Among solvent extraction systems developed and applied to the separation of actinide(III) ions, An(III), and lanthanide(III) ions, Ln(III), a synergistic extraction is advantageous to enhance the extraction efficiency of these ions having high coordination numbers. Many synergistic extraction systems have been proposed [1–3], but the selectivity in these systems is usually not improved despite the higher extractability. We have found [4,5] that An(III) and Ln(III) were extracted using 2-thenoyltrifluoroacetone (HTTA) and 18-crown-6 ether (18C6) through competitive reactions. One of the competitive reactions is a synergistic ion-pair extraction (SIPE) of Am^{3+}, Cm^{3+}, and the lighter Ln(III), e.g., La^{3+}–Tb^{3+}, as a cationic complex into 1,2-dichloroethane (DCE) or nitrobenzene of relatively high dielectric constant. The cationic complex extracted by SIPE was determined to be $M(TTA)_2(18C6)^+$, M(III)= An(III), Ln(III). Another competitive reaction is a generally accepted synergistic extraction (SE) to extract a neutral complex $M(TTA)_3(18C6)$ into nonpolar solvents such as benzene (Bz) or cyclohexane. It was observed that M(III) having ionic diameter close to the cavity size of 18C6 was extracted more efficiently through SIPE and the separation factor of adjacent elements was enhanced markedly. Either SIPE or SE is predominant in a given system depending on the kind of crown ether and β-diketone as well as on their concentrations. We have assumed that a steric effect of β-diketone plays an important role in the predominancy of the formation of $M(TTA)_2(18C6)^+$- or $M(TTA)_3(18C6)$-type complexes. In the present work, the extraction behavior of Am^{3+}, Cm^{3+} and Ln^{3+} have been investigated-with DCE containing 18C6 and the β-diketone (HA), trifluoroacetylacetone (HTFA), HTTA, benzoyltrifluoroacetone (HBFA), or 2-naphthoyltrifluoroacetone (HNFA).

2. Experimental

Stock solutions of An(III) were prepared from ^{241}Am (Amersham) and ^{244}Cm (CEA) [4]. The radioisotopes of Ln(III) were produced by neutron irradiation and the stock solutions of 10^{-5}–10^{-3} M Ln(III) were prepared by mixing the radioactive tracer with the carrier of the respective Ln(III) salts [5]. The HTFA (Dojindo Lab.) was purified by distillation and HTTA, HBFA (Dojindo) and HNFA (Aldrich) were purified by sublimation. The 18C6

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(Aldrich) was purified by recrystallization. The distribution ratio of metal ion between aqueous and DCE solutions was determined by the measurement of radioactivities in both phases after the extraction equilibrium [4,5]. All measurements were performed at 24±1°C.

3. Results

Distribution ratios D were determined for the extraction of M(III) in 0.1 M $LiClO_4+10^{-3}$ M acetate buffer of various pH with DCE containing 0.01 M HTFA, HTTA, HBFA, or HNFA together with 0.01 M 18C6. In order to clarify the steric effect of β-diketones, four β-diketones were selected taking into consideration that these reagents have similar acid dissociation constants [6,7], $pK_a=6.4$ (HTFA), 6.2 (HTTA), 6.3 (HBFA) and 6.3 (HNFA), and have substituent groups of different bulkiness at their γ-position. The molar volume of HA was calculated to be 118 (HTFA), 143 (HTTA), 156 (HBFA) or 184 (HNFA) cm^3/mol on the basis of the additivity of partial molecular volume [8].

Log D vs. pH plots for the extraction of Am^{3+} and Gd^{3+} are shown in Figs. 1 and 2.The dotted lines in the figures are log D_0 vs. pH plots for the extraction with 0.01 M HA in the absence of CE. There is a remarkable synergistic effect by 18C6, showing the increase of D at a given pH, observed for all HA examined. Log D vs. pH plots for Am^{3+} show clear linearity with slopes of 1.7 (HTFA), 2.1 (HTTA), 1.9 (HBFA) or 1.9 (HNFA). It can be concluded that Am^{3+} is extracted predominantly through SIPE, as Eq. (1), regardless of the kind of β-diketone.

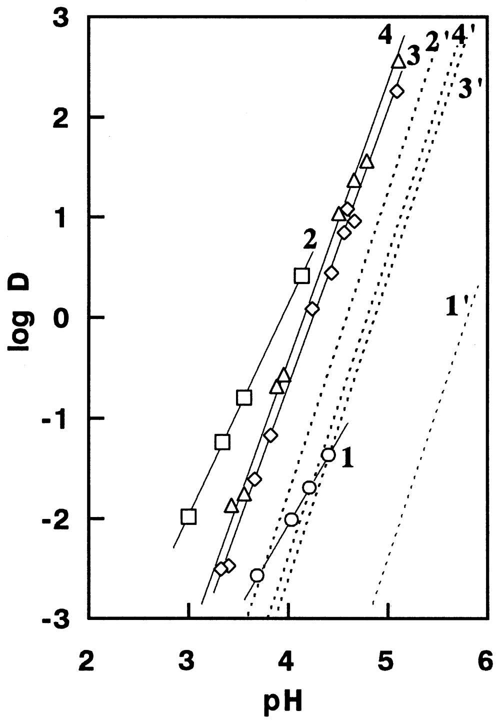

Fig. 2. Log D–pH plots for the extraction of Gd^{3+} using DCE with β-diketone and 18C6. Aqueous solution: 0.1 M $LiClO_4+10^{-3}$ M acetate buffer; DCE solution: (1–4) 0.01 M HA+0.01 M 18C6, (1′–4′) 0.01 M HA; HA: (1,1′) HTFA, (2,2′) HTTA, (3,3′) HBFA, (4,4′) HNFA.

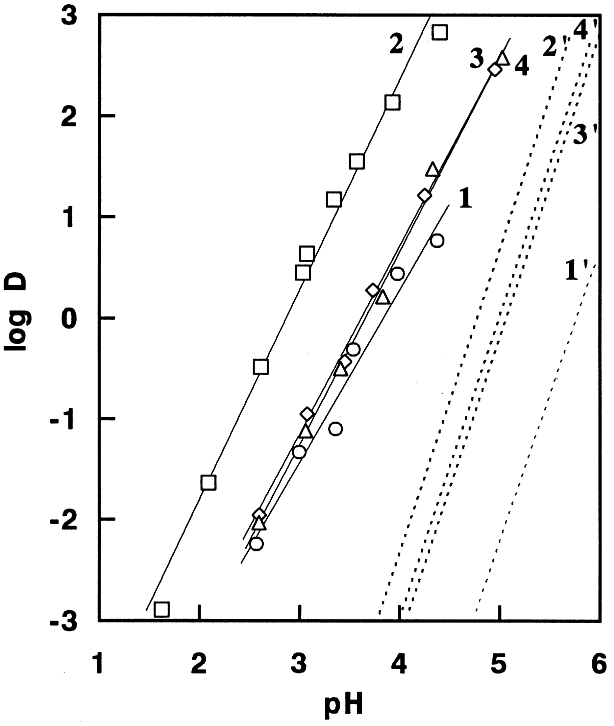

Fig. 1. Log D–pH plots for the extraction of Am^{3+} using DCE with β-diketone and 18C6. Aqueous solution: 0.1 M $LiClO_4+10^{-3}$ M acetate buffer; DCE solution: (1–4) 0.01 M HA+0.01 M 18C6, (1′–4′) 0.01 M HA; HA: (1,1′) HTFA, (2,2′) HTTA, (3,3′) HBFA, (4,4′) HNFA.

$$M^{3+} + 2HA_{org} + 18C6_{org} + ClO_4^- \rightleftharpoons MA_2(18C6)^+_{org} + ClO^-_{4org} + 2H^+ \quad (1)$$

The slopes of log D vs. pH plots for Gd^{3+} are 1.7 (HTFA), 2.1 (HTTA), 2.7 (HBFA) or 2.8 (HNFA). Gadolinium(III) is extracted through SIPE using HTFA or HTTA with relatively small substituent groups, and extracted through SE, Eq. (2), using HBFA or HNFA.

$$M^{3+} + 3HA_{org} + 18C6_{org} \rightleftharpoons MA_3(18C6)_{org} + 3H^+ \quad (2)$$

The slopes of log D vs. pH plots for M(III) are summarized in Table 1. The slopes 2±0.3 and 3±0.3 imply that M(III) is extracted predominantly through SIPE and SE, respectively. In log D vs. pH plots for the extraction of Eu^{3+} with HNFA and Tb^{3+} with HTTA, two linear portions with different slopes of 2 and 3 are observed. These results suggest that both SIPE and SE can be observed in the extraction of Eu^{3+} with HNFA and Tb^{3+} with HTTA depending on pH. With HA of relatively

Table 1
The slopes of log D vs. pH plots for the extraction of M(III) into DCE with 0.01 M HA and 0.01 M 18C6

	HA			
Element	HTFA	HTTA	HBFA	HNFA
Am^{3+}	1.7	2.1	1.9	1.9
Cm^{3+}	1.6	1.9	1.8	1.9
Nd^{3+}	1.9	1.9	2.0	1.9
Pm^{3+}	2.1	1.9	1.9	1.9
Sm^{3+}	1.8	2.0	2.0	2.0
Eu^{3+}	1.7	2.0	2.2	2.3, pH$<$3.8 2.7, pH$>$4.2
Gd^{3+}	1.7	2.1	2.7	2.8
Tb^{3+}	1.7	2.2, pH$<$3.5 3.0, pH$>$4.0	2.7	2.8

small substituent groups SIPE occurs predominantly, and with HA of larger substituent SE becomes predominant. The SE reaction is predominant for the extraction of the heavier Ln(III).

Distribution ratios at pH$=$3, $D_{\mathrm{pH}=3}$, obtained for the extraction through SIPE were determined and the results are listed in Table 2. Values with asterisk are those obtained by the extraction through SE instead of SIPE. The separation factors, $\alpha_{\mathrm{I/II}}$, between M_I and M_{II} of adjacent An(III) or Ln(III) pair; $\alpha_{\mathrm{I/II}}=D_I/D_{II}$, were calculated and are summarized in Table 3. In addition, the separation factors $\alpha_{\mathrm{Am/Ln}}$ and $\alpha_{\mathrm{Nd/Ln}}$, which are of particular interest for the nuclear technology [9], were calculated as an indication of the selectivity for the separation of Am^{3+} or Nd^{3+} from the other Ln(III). For the comparison, the separation factors for extraction into DCE with HTTA in the absence of CE, $\alpha_{\mathrm{I/II(HTTA)}}$, are added to Table 3 [4,5]. The $\alpha_{\mathrm{I/II}}$ obtained by SIPE with HTTA is obviously larger than $\alpha_{\mathrm{I/II(HTTA)}}$. In this particular case, $\alpha_{\mathrm{Am/Tb}}$ is almost 50 times larger than $\alpha_{\mathrm{Am/Tb(HTTA)}}$. The $\alpha_{\mathrm{I/II}}$ for SIPE are 2–7 and do not show clear dependence on the kind of HA. The average of $\alpha_{\mathrm{I/II}}$ of Ln(III) is 3.6 (HTFA), 3.1 (HTTA), 2.3 (HBFA) or 2.7 (HNFA). One of the highest selectivities in the separation of Ln(III) was reported to be 2.5 of the average $\alpha_{\mathrm{I/II}}$ [10] which was observed in the extraction using HDEHPA. It is noteworthy that $\alpha_{\mathrm{Am/Ln}}$ and $\alpha_{\mathrm{Nd/Ln}}$ for the heavier Ln(III) are highly enhanced. The extent of the increase of $\alpha_{\mathrm{Am/Ln}}$ and $\alpha_{\mathrm{Nd/Ln}}$ is more remarkable with HA of smaller substituent group.

Table 3
The separation factors between M_I/M_{II}

M_I/M_{II}	HA HTFA	HTTA	HBFA	HNFA
Am^{3+}/Cm^{3+}	6.0	4.2 [1.4^a]	5.1	6.2
Nd^{3+}/Pm^{3+}	2.5	2.6 [1.8^a]	2.4	2.1
Pm^{3+}/Sm^{3+}	2.7	3.8 [1.5^a]	2.1	2.2
Sm^{3+}/Eu^{3+}	6.6	2.5 [1.5^a]	2.4	4.1
Eu^{3+}/Gd^{3+}	5.4	5.5 [2.0^a]	–	$(1.3)^a$
Gd^{3+}/Tb^{3+}	2.3	2.1 [1.6^a]	$(1.1)^a$	$(1.5)^a$
Nd^{3+}/Sm^{3+}	6.9	9.8 [2.7^a]	5.2	4.6
Nd^{3+}/Eu^{3+}	45	25 [4.0^a]	12	19
Nd^{3+}/Gd^{3+}	247	136 [8.1^a]	–	–
Nd^{3+}/Tb^{3+}	566	284 [13^a]	–	–
Am^{3+}/Nd^{3+}	1.3	1.1 [2.0]	1.9	1.2^a
Am^{3+}/Pm^{3+}	3.4	2.9 [1.1]	4.5	1.8
Am^{3+}/Sm^{3+}	9.1	11 [1.3^a]	9.8	3.9
Am^{3+}/Eu^{3+}	60	28 [2.0^a]	24	16
Am^{3+}/Gd^{3+}	327	154 [4.1^a]	–	–
Am^{3+}/Tb^{3+}	752	321 [6.5^a]	–	–

[a] M_{II}/M_I.
( ): In the extraction through SE.
[ ]: In the extraction by HTTA in the absence of 18C6.

4. Discussion

Structural information on the extracted metal complexes are helpful for elucidating the steric effect of HA in the synergistic extraction of M(III) with HA and 18C6. The determination of the number of coordinated water molecules of complex extracted may provide a powerful insight into the configuration of complexes. We determined [11] the number of water molecules in the first coordination sphere of Eu^{3+} in the $Eu(TTA)_2(18C6)^+$ complex extracted in DCE and $Eu(TTA)_3(18C6)$ in Bz by time-resolved laser-induced luminescence spectroscopy. It was found that the cationic complex had 2 water molecules and the neutral complex had 1–2 water molecules. Taking into account that the coordination number of Eu^{3+} is often 9, 18C6 may combine with Eu^{3+} occupying three coordination sites of Eu^{3+} in $Eu(TTA)_2(18C6)^+$, and 1–2 coordination sites in $Eu(TTA)_3(18C6)$. It is assumed, therefore, that 18C6 behaves as a multidentate adduct in $Eu(TTA)_2(18C6)^+$ and as a monodentate adduct in $Eu(TTA)_3(18C6)$.

As shown in Table 1, SE reaction is predominant in the extraction of the heavier Ln(III) with HA of the larger

Table 2
Log D at pH 3 for SIPE of M(III) into DCE with 0.01 M HA and 0.01 M 18C6

	Am^{3+}	Cm^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}
HTFA	−1.57	−2.35	−1.70	−2.10	−2.53	−3.35	−4.09	−4.45
HTTA	0.27	−0.36	0.21	−0.20	−0.78	−1.18	−1.92	−2.24
HBFA	−1.24	−1.95	−1.52	−1.90	−2.23	−2.61	-3.74^a	-3.68^a
HNFA	−1.31	−2.11	−1.24	−1.56	−1.90	−2.51	-3.52^a	-3.36^a

[a] Extraction through SE.

substituent. This suggests that steric hindrance by the bulky substituent group prevents the formation of the multidentate M(III)-18C6 bonds for the heavier Ln(III) and results in the formation of $MA_3(18C6)$. In the extraction of the lighter Ln(III), Am^{3+} and Cm^{3+}, SE reaction was not observed even with HA of the larger substituent. This result can be interpreted by the stabilization of multidentate M(III)-18C6 bonds due to so-called size-fitting effect between the cavity size of 18C6 and the ionic size of these metal ions. We reported previously that high extractability as well as high selectivity in SIPE was attributable to size-fitting effect between 18C6 and the lighter Ln(III) [5], Am^{3+} or Cm^{3+} [4].

The separation factor $\alpha_{I/II}$ observed in SIPE extraction is larger than $\alpha_{I/II(HTTA)}$ in the HTTA-extraction without 18C6, which can be elucidated considering that multidentate M(III)-18C6 bonds in $M(TTA)_2(18C6)^+$ allows an effective differentiation of the ionic size of An(III) or Ln(III). The influence of the nature of HA on the separation factor is clearly observed in the results of $\alpha_{Nd/Ln}$ and $\alpha_{Am/Ln}$ (Table 3). The smaller steric effect due to HA with small substituent groups results in larger separation factors, since the steric hindrance by HA is small enough to allow an effective size-fitting.

5. Conclusion

Synergistic ion-pair extraction, SIPE, of $MA_2(18C6)^+$ type complex of An(III) or Ln(III) using β-diketone and crown ether is advantageous for separating metal ions efficiently and selectively. The $MA_2(18C6)^+$ complex involving multidentate M(III)-18C6 bonds adopts a configuration in which the size fitting between the ionic diameter of M(III) and the cavity size of CE works effectively. The result of the present investigation suggests that using HA with the smaller substituent groups leads to smaller steric hindrance, and allows an efficient SIPE pathway and even an increase in the selectivity of the intra- and inter-group separation of An(III) and Ln(III).

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